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Oxetane Photopolymerization - A System With Low Volume Shrinkage

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Abstract

Several mono-, bi- and trifunctional oxetanes were synthesized and polymerized in bulk and in solution cationically. Selected photoinitiators have been applied. It was found that sulfonium salts are very efficient due to good solubility, almost no discolouration of the product and storage stability in the monomer in the absence of light. The conversion was determined by quantitative IR-spectroscopy. Conversion between 75% and 85% was found in all cases. The shrinkage during polymerization was much lower than for vinyl monomers. No inhibition by oxygen was recognized. Monomer layers thicker than 5.5 mm could be polymerized. The products are transparent and almost colourless. The glass transition temperature of the crosslinked polymers was above the temperature of a human body.

1. Introduction

Many monomers used in the manufacture of commercially available polymeric compositions such as casting resins, molding resins, film coatings etc. exhibit some degree of shrinkage during manufacturing and processing. Shrinkage is defined as the reduction in volume brought about by an increase in density, which is observed during polymerization and polymer cure. One of the main causes of shrinkage is that in the monomer, the molecules are located at a Van der Waals distance from one another, while in the polymer, the corresponding monomeric units move into the shorter covalent distance of one another. Less important, but still significant factors which affect volume shrinkage are the change in entropy during polymerization, free volume in amorphous polymers and how well the monomer and polymer pack if crystals are present in either phase [1].

If the polymerization is incomplete small quantities of unreacted monomer are present in the finished product. Further reaction or migration of the monomer can occur during thermal aging. In both cases one would observe additional shrinkage.

Polymerization shrinkage can produce internal compressive stress, which can cause of microcracks and microvoids. In molding application polymer shrinkage results in incomplete filling of the mold and poor replication of the mold surface. It is quite obvious that elimination or significant reduction of the polymerization shrinkage would result in better polymeric products. This presentation will concentrate on a system valid for dental applications and resins as alternatives for inlay and amalgam filling for teeth.

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2. Methods to reduce shrinkage in volume

2.1. Fillers

Addition of fillers to the monomer or monomer mixture is the simplest and probably the cheapest method to reduce the shrinkage during polymerization. If 80% of the mixture is filler, the overall shrinkage of this composite is reduced to 20% of the original value. The shrinkage of MMA (21.2%) can be reduced to 4.2% if the monomer is filled with 80% quartz.

2.2. Large monomers and prepolymers

Increasing molar mass per polymerizable group reduces the overall shrinkage effect:

Ethylene:	$\Delta V = 66.0\%$	(M = 28.1)
Methyl methacrylate:	$\Delta V = 21.2\%$	(M= 100.1)
N-Vinylcarbazole:	$\Delta V = 7.4\%$	(M = 193.3)

Therefore it is quite logical to apply prepolymers and oligomers with reactive functional groups for chain extension or crosslinking.

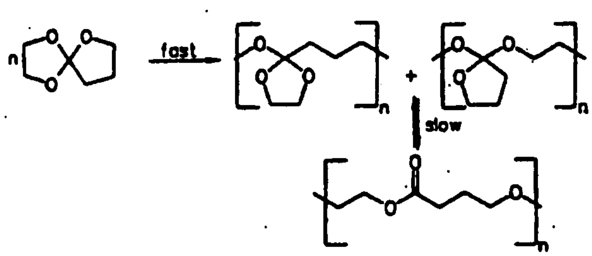
2.2. Ring-opening polymerization

An elegant route to avoid or to reduce shrinkage during polymerization is the ring-opening polymerization. For one new covalent bond in the polymer at least one bond in the corresponding monomer has to be broken.

Monomers with reduced shrinkage are:

- cyclic ethers
- saturated nitrogen heterocycles
- lactones, lactames
- cyclic carbonates
- stressed aliphatic rings

Much attention was paid to double ring-opening of spiro ortho carbonates and spiro ortho esters, which show volume extension during polymerization [1,2].



2.3. Polymerization of organized structures

Although this group of organized monomers (crystallized or those with LC phases) is of no importance for dental application it should be mentioned here for completeness. For example, solid state polymerization of acetylenes and cyclodimerization of α,β-unsaturated carbonyl compounds

are only possible if the reacting monomers are close enough to each other [7]. Reduced shrinkage was also observed for acrylate-type monomers with LC properties [9].

2.4.Conclusion

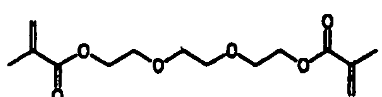
Fillers and large monomers and their combinations are the favoured systems in dental applications for reduced shrinkage during polymerization. Cylic and bicyclic compounds are certainly interesting, however, they still wait for commercialization due to many reasons (they are expensive; their volume expansion during polymerization is questionable; resulting polymers show often poor properties...). Looking more closely at the cyclic ethers and at the requirements for a system for dental applications it seemed worthwhile to include those compounds into the list of alternative systems to acrylates and methacrylates.

3. Light curing composites for dental applications

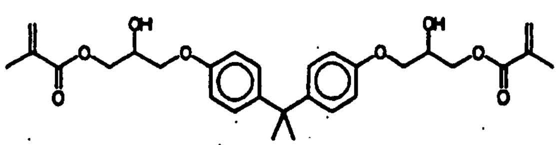
3.1. Classical composites

The basic components for dental composites are
- monomer
- filler
- initiator
- stabilizer

Monomers are bi- and trifunctional methacrylates with low viscosity [1,6]. Typical examples are Bis-GMA and TEDMA:



TEDMA



Bis-GMA

Fillers are based on inorganic material which are not only variable in nature but also in size. A typical classification is:

course-grained fillers (> 30μm): quartz powder, aluminium oxide, boric oxide, phoshates
refined fillers (1-30μm): amorphous silicates, different SiO_2 glasses, aluminium oxide
ultra-refined fillers (0.005 - 0.05μm): ultra refined SiO_2 made by pyrolysis of silanes and siloxanes

Silanation of the surface of fillers with methacryltrimethoxysilanes improves the properties of fillers and their interconnection in the resulting polymer.

It is most common to apply photoinitiators and to induce the polymerization by UV/Vis-light [3,7,8)]. Important initiators are camphorquinone and benzoin alkyl ether. All of them decompose via radical intermediates.
As stabilizer derivatives of cresols such as Junole(2,6-di-tert-butyl-4-methyl-phenol) are often used in dental formulations.

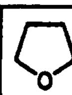
3.2 Formulations based on cyclic ethers

Before we discuss the properties and polymerization behavior of cyclic ethers in some detail it is necessary to look at the list of requirements for the new generation of dental composites:

1. low shrinkage or expansion in volume during polymerization
2. light induced polymerization
3. no inhibition of the polymerization by oxygen
4. simple and cheap synthesis of the monomers
5. simple workability of the monomers
6. non-toxicity
7. monomers must be bi-or higher functional
8. low water adsorption of the polymers
9. the resulting products must be transparent which must not change their colour

It is not unlikely that this list must be extended in the future.
Suitable candidates of cyclic ethers for dental application are listed in the following table:

Table 1: selected properties of cyclic ethers

			
molecular weight	44.1	58.1	72.1
density /(g·mL^{-1})	0.882	0.893	0.889
decrease in vol.-%	23	17*	10
pK_a	- 3.7	- 2.02	- 2.1
ring strain /(kJ·mol^{-1})	114	107	23

* *estimated in relationship of oxirane and tetrahydrofuran*

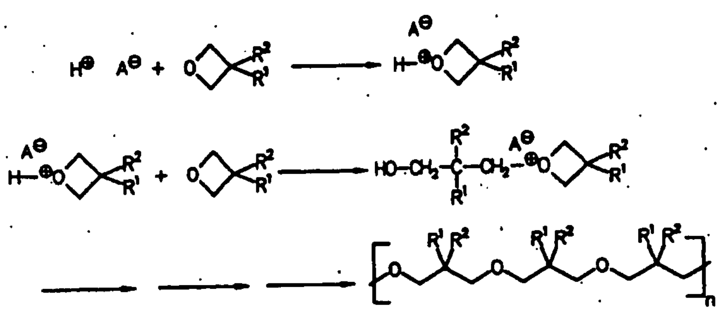
From monomers containing oxetane units we expect less shrinkage in volume than from MMA. Oxetanes are easy to synthesize and can be polymerized cationically by photoinitiators such as sulfonium and iodonium salts, undisturbed by oxygen and little affected by moisture [9-11)]. The monomer synthesis is rather simple [12)]. The resulting polymer contains ether function and is less hydrophobic than PMMA. A further advantage is that the polymer is free of C,C- double bonds

even at incomplete conversion of the monomer. No information was available on the degree of shrinkage in volume during polymerization. However, a very rough estimate (see Table 1) shows that it is remakably lower than for MMA.
Most Important factors which control the reactivity of the rings are basicity of the ring oxygen, ring stress and sterical hindrance. Since ring stress is similar for oxiranes and oxetanes but basicity is higher for oxetanes we consider oxetanes an interesting family of compounds for applications in which reduced shrinkage in volume is important [13].

4.Cationic polymerization of oxetanes

4.1. Classical methods

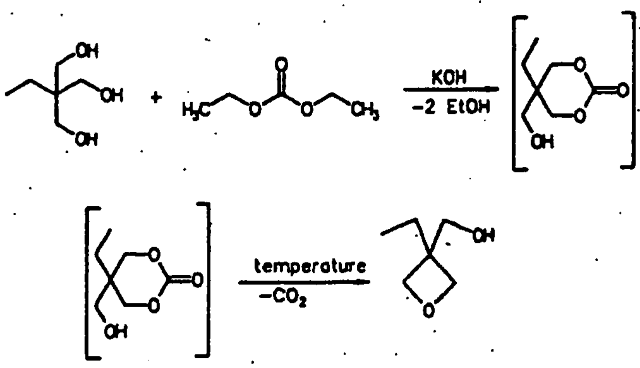
Ring-opening polymerization of oxetanes can be initiated by means of protonic acids[14], oxonium salts [15], hexafluorophosphates [16] and Lewis acids in the presence of coinitiators [17-19]. Side reactions such as ring formation and backbiting can be reduced by lowering the reaction temperature [20,21]. These reactions can be more or less ignored in case of dental composites if bi- and higher functional monomers are applied.



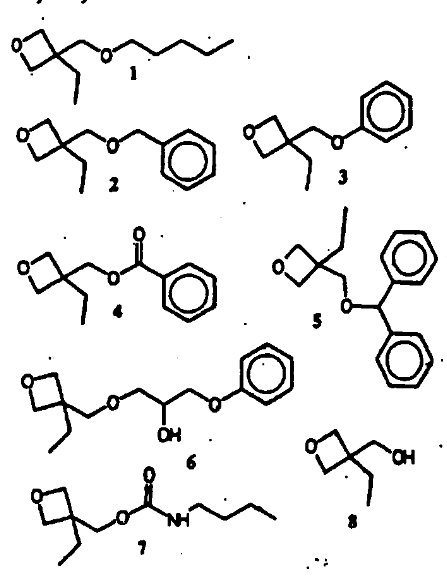
Linear polyoxetanes were synthesized as early as 1954 [22,23] and became commercial products (3,3-bis(chloromethyl)oxetane: *Penton*, *Pentaplast*) which show mechanical properties comparable with nylon-6 and a remarkable chemical resistance [24].

4.2. Monofunctional monomers

The simplest and probably cheapest method for the synthesis of monofunctional oxetane is the transesterification of diethyl carbonate with 1,1,1-trimethylolpropane yielding a cyclic carbonate as intermediate which split off CO_2 to form 3-ethyl-3-hydroxymethyloxetane [13].



3-Ethyl-3-hydroxymethyloxetane is the basis for most of the monomers listed below:



Phenylether 3 was synthesized by reaction of phenol with 3-chloromethyl-3-ethyloxetane which is available from 1,1,1-trimethylolpropane by reaction with $SOCl_2$ followed by ring formation accompanied with HCl abstraction.

The monomers are completely characterized by common analytical methods. It is interesting to note in which way ^1H NMR spectra of 3-chloromethyl-3-ethyloxetane differ from the spectra of 3-ethyl-3-hydroxymethyloxetane:

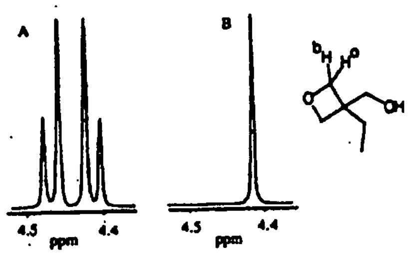


Figure 1: Section of the ^1H NMR spectra of 3-ethyl-3-hydroxymethyloxetane (A) and 3-chloromethyl-3-ethyloxetane (B).

Since the oxetane ring is not completely planar, one can distinguish between H_a and H_b for 3-ethyl-3-hydroxymethyloxetane due to the stabilization of the ring conformers by hydrogen bridging which is not possible for the 3-chloromethyl-derivative that is why in the last case a singulet is observed.

4.3. Polymerization rate

The polymerization of the monofunctional monomers were studied by means of ^1H NMR with $BF_3 \cdot OEt_2$ as initiator:

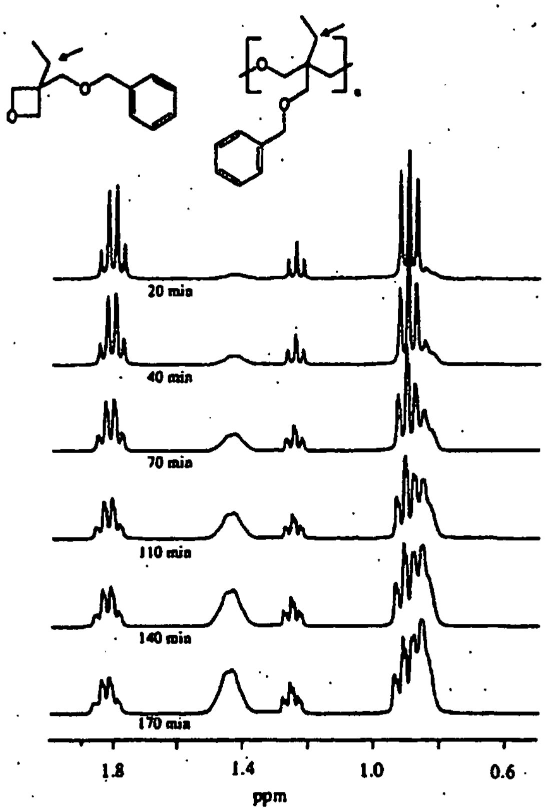


Figure 2: ^{1}H NMR of 2, rate of polymerization initiated by $BF_3 \bullet OEt_2$, T = 27 °C

Quantitative data are given in the following table:

Table 2: Polymerization of different oxetanes in $CDCl_3$ solution, monomer concentration = 0.41 mol·L^{-1}, initiated by $BF_3 \cdot OEt_2$ (c = 0.041 mol·L^{-1}), T = 27 °C

monomer		polymerization rate[1] mol·min^{-1}·L^{-1}·10^{-3}	formation of cycles and oligomers
Benzyl ether I	2	2.5	-
Phenyl ether	3	3.0	-
Alkyl ether	1	2.8	-
Benzyl ether II	5	6.1	-
Ester	4	6.3	+
Urethane	7	no polymerization	
Alcohol	8	11.6	-
Hydroxyl ether	9	9.3	-

[1] *linear regression (20 % conversion)*

It is interesting to note that the highest rates of polymerization were observed for monomers which contain hydroxy groups or labile hydrogens (Benzyl ether II). Esters and urethane are either non-polymerizable or react with very low rates only. This can easily be explained on the basis of their pK_a-values:

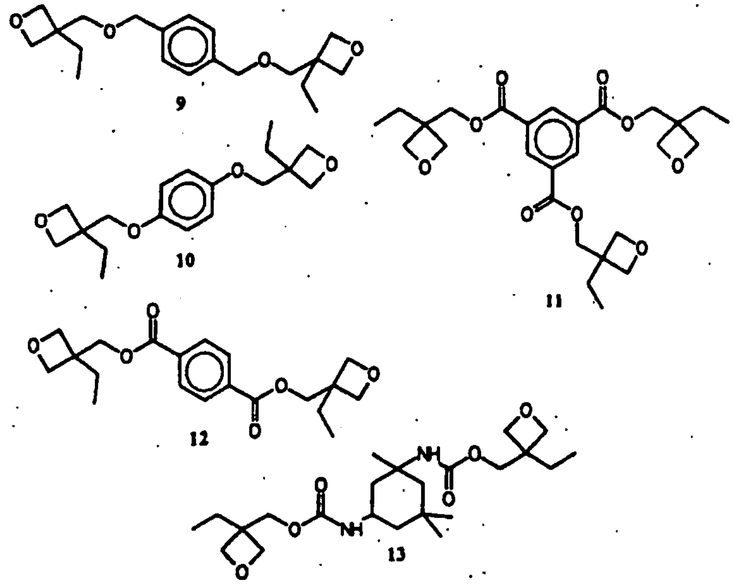
Table 3: pKa-values of selected compounds having functional groups similiar to 1-8

compound	pK_a -value
Ethyl phenyl ether	- 6.44
Diethyl ether	- 3.59
Methanol	- 2.20
Isopropanol	- 3.20
Ethyl benzoate	- 7.78
N-Methylacetamide	- 0.46
Alcohol 8	- 2.08

Those functional groups are problematic which have pK_a-values higher (less negative) than that of oxetane, which is in agreement with our experimental results.
The relatively low molar masses for the polymers from hydroxy containing monomers indicate that OH interfers with the reaction yielding oxonium groups, which stabilize via proton transfer.

4.4. Bi- and trifunctional oxetanes

The route for the preparation of the bi- and trifunctional monomers listed below is adapted from that of the monofunctional monomers:



9, 10, 11, 12, 13

All these monomers are solids. However, they can be converted into the liquids by addition of traces of monofunctional oxetanes.
Different photoinitiators have been tested for the cationic polymerization of selected oxetanes: Sulfonium salt [25], iodonium salt [26], N-oxide [27], metal complex [28] and sulfonic acid ester [29].
Without going into too many details one can summarize the tests of initiators in the following way: All tested sulfonium and iodonium salts were initiators for oxetanes. However, only Degacure KI 85B fulfilled all the requirements: fast reaction, suitable solubility, almost no discolouration of the product, storage stability dissolved in the monomer (avoiding light).

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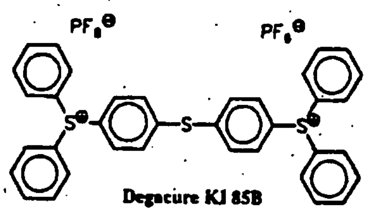

Degacure KI 85B

The following mechanism was proposed for the photodecomposition of the initiator[30]:

$$Ph_3S^{\oplus}\,X^{\ominus} \xrightarrow{h\nu} [Ph_3S^{\oplus}\,X^{\ominus}]^{*}$$
$$[Ph_3S^{\oplus}\,X^{\ominus}]^{*} \longrightarrow [Ph_2S + Ph^{\oplus}\,X^{\ominus}]$$
$$[Ph_2S + Ph^{\oplus}\,X^{\ominus}] \longrightarrow Ph_2S + Ph^{\oplus} + X^{\ominus}$$
$$Ph^{\oplus} + R{-}H \longrightarrow Ph{-}R + H^{\oplus}$$

The light induced polymerization of the bifunctional oxetanes was studied in bulk with a commercial UNILUX AC (Kulzer). The monomer/initiator was filled in a special designed cell, shown in the following figure:

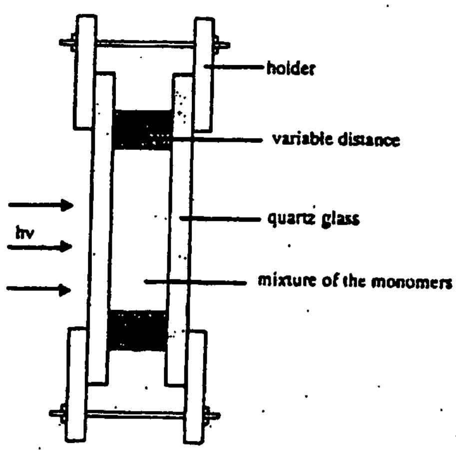

Figure 3: Cell for photo-polymerization of the oxetanes

From quantitative IR (integrating the residual peak or determination of the residual peak hight), monitoring the consumption of the COC-bond at 980 cm^{-1}, we know that 75 to 85% of the monomer was converted into polymer under the experimental conditions in less then 2- 5 minutes depending on the thickness of the monomer layer.

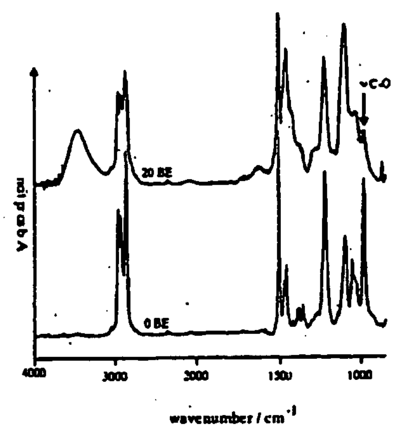

Figure 4: IR-spectra of an oxetane (dibenzyl ether 9) before (0 BE) and after (20 BE) irridiation
BE : irridiation units (Belichtungseinheiten)

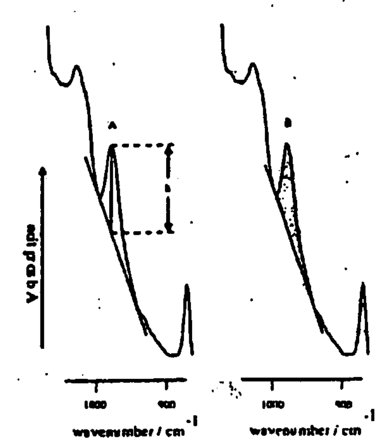

Figure 5: Quantitative IR (A: height method, B: area method)

It is also importent to note that the glass transition temperature of the polymers reached an acceptable level above the temperature of a human body.

5. Shrinkage in volume

On the basis of theoretical consideration we expected a reduced shrinkage of the oxetanes compared to MMA. The experimental results fully support the expectation. From monomer and polymer densities the shrinkage can be calculated by using the following equation:

$$Shrinkage\,/\,\% = \frac{\rho_M - \rho_P}{\rho_M} \cdot 100\%$$

ρ_M = density of the monomer

ρ_P = density of the polymer

Some of the results are given in the following table

Table 4: Shrinkage in volume of selected oxetanes

monomer	$\rho_{monomer}$ g cm^{-3}	$\rho_{polymer}$ g cm^{-3}	shrinkage %	conversion %
Alcohol 8	1.0209	1.10	7.8	100
Benzyl ether 2	1.0236	1.07	4.9	100
Dibenzyl ether 9	1.0657	1.11	3.9	70 - 80

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